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WASTE DISPOSAL STUDY. EVALUATION OF METHODS TO RECOVER REUSABLE--ETC(U)
SEP 76 G A LORENZO, T N HENDRICKSON

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**WASTE DISPOSAL STUDY
EVALUATION OF METHODS TO RECOVER REUSABLE
CHEMICALS FROM EVAPORATED PHOTOWASTES**

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CPAC, INC.
POLLUTION ABATEMENT DIVISION
LEICESTER, NEW YORK 14451

SEPTEMBER 1976



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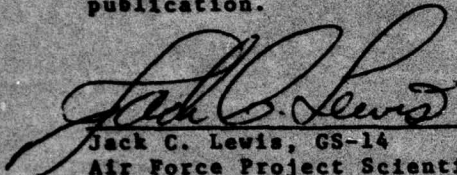
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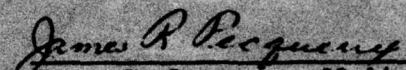
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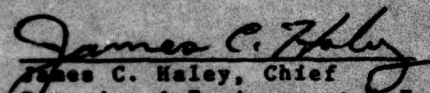
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The feasibility of recovering usable chemicals from evaporated photoprocess- ing wastes was studied. About 50-70% of the evaporated waste consists of sodium thiosulfate and sodium sulfite. The expected organic chemicals (especially developers) were present in such low concentrations that recov- ery was unjustified. (Con't. next page)			

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Recovery of thiosulfate and sulfite was achieved via solubilization and either a combination of crystallization and subsequent barium precipitation of these desired sulfur salts, or direct barium precipitation. The barium salts could then be converted to the soluble sodium thiosulfate and sodium sulfite by action of sodium carbonate. Recovery efficiencies to 90% were achieved.

Maximum yields were obtained when the sodium thiosulfate was greater than 50% of the waste, and water was used as the solubilizing agent. For wastes containing quantities lower than this concentrate, sodium hydroxide was the solvent of choice. The latter allowed separation of sulfite from thiosulfate.

Results indicate that recovery of major chemicals is feasible and can be economically justified. Scale-up to pilot plant is recommended.

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PREFACE

Gratitude is expressed to Dr. Charlton C. Bard, Photographic Technology Division, Eastman Kodak Company, for several enlightening discussions concerning the expected chemical nature of photographic wastes and for infrared spectra of some sulfonated developers.

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SECTION I

INTRODUCTION

1. Background

In an effort to reduce the potentially harmful effect of photographic processing effluents on the environment, the U.S. Government has investigated methods of treating such water wastes. One approach involves evaporation of the solutions containing the undesirable chemicals. In that process only evaporated water is discharged. The toxic photoprocessing chemicals are isolated in a slurry or solid with low water content. An evaporation unit was placed into operation at an Air Force facility to determine operating efficiencies with photographic processing wastes.

The resulting solid evaporated waste is considered to be a disposal problem. Current and anticipated Federal Government regulations may not allow disposal to landfill or other dumping areas.

2. Purpose

The major purpose of this study was to determine the most practical method of disposal of waste products generated as a result of the evaporation of photographic solutions.

This report describes an investigation into the feasibility of treating the evaporated solid for reuse of certain chemicals. The purity of the recovered compounds would dictate that segment of industry capable of absorbing these recycled chemicals.

Preferential consideration was given to the reclamation of all or part of the chemical waste rendering it suitable for use by a segment of industry capable of absorbing the total quantity of these chemicals. Lower priority factors in order of importance included the conversion of all or part of the waste into:

- 1) insoluble materials of construction,
- 2) harmless gases for release into the atmosphere,
and/or
- 3) a form acceptable to conventional sewage treatment plants.

Theory: The Proposed Recovery Scheme

Chemical treatment was proposed as a possible method of reclamation for evaporated solids. The simplicity of the method and the types and cost of chemicals used were important factors in this choice.

Two approaches were considered:

- 1) To treat the desired compounds chemically for conversion to compounds that are more easily removed, or
- 2) to chemically treat the undesired compounds for removal from the desired chemicals.

The former approach is preferred when the undesired compounds are numerous and complex, as with an evaporated photo waste.

Table 1 shows projected composition of an evaporated black-and-white waste as provided by the Air Force. Sodium thiosulfate and sodium sulfite together comprise about 66% of the dry weight.

TABLE 1

WATER-FREE COMPOSITION OF BLACK-AND-WHITE PHOTOCHEMICALS
(As Estimated by the Air Force)

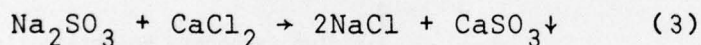
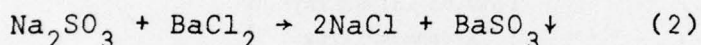
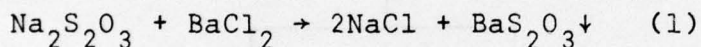
<u>Chemical</u>	<u>% by Weight</u>
Sodium Thiosulfate	33.33
Sodium Sulfite	32.74
Sodium Metaborate	17.95
Acetic Acid	7.73
Para-Aminophenol	2.62
Potassium Alum	2.06
Sodium Hydroxide	1.51
Hydroquinone	1.40
Sodium Bisulfite	0.27
Potassium Bromide	0.27
Hexameta Sodium Phosphate	0.114
Alkyl Benzenesulfonate	<u>0.002</u>
Total	99.996

This estimate was made from known compositions of solutions in processing and does not take into account decomposition by either chemical interaction or heating during evaporation.

Projections were also provided on the chemical composition of evaporated wastes generated from the processing of color photographic products and the combination of both black-and-white and color. The color only composition estimated 17.1% sodium sulfite and 3.5% sodium thiosulfate.

The combination waste was estimated at 24.8% sodium sulfite and 18.5% sodium thiosulfate.

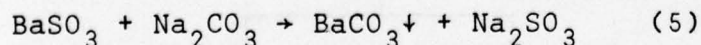
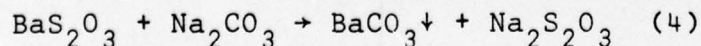
The steps proposed for reclaiming the major chemicals, thiosulfate and sulfite, from the evaporated solid waste were based upon the solubility products of the compounds and their potential for reuse in the open market. The proposed recovery scheme is shown in Figure 1. The first step is to solubilize the evaporated solid waste. That is followed by precipitation of the sulfite and thiosulfate to isolate those compounds. The low solubility of the barium salts of these compounds resulted in the initial choice of barium ion (Ba^{+2}) as the precipitating agent. Calcium was considered for precipitation of the sulfite. Equations (1), (2) and (3) show the reactions expected.



Barium thiosulfate (BaS_2O_3) has a solubility in water of 0.2 grams per 100 grams of water while barium sulfite ($BaSO_3$) has a solubility of 0.02 grams per 100 grams of water.

Other chemical species were expected to precipitate with barium, depending on the conditions of the reaction. Barium borate, barium carbonate, barium phosphate and barium sulfate may also be present in the precipitate.

Once isolated, barium thiosulfate and barium sulfite must be converted to their sodium salts prior to reuse in the photographic process. The action of a concentrated sodium carbonate solution was chosen for that purpose (Equations 4 and 5).



The choice of sodium carbonate is enhanced by the fact that it also serves to remove barium from solution as barium carbonate.

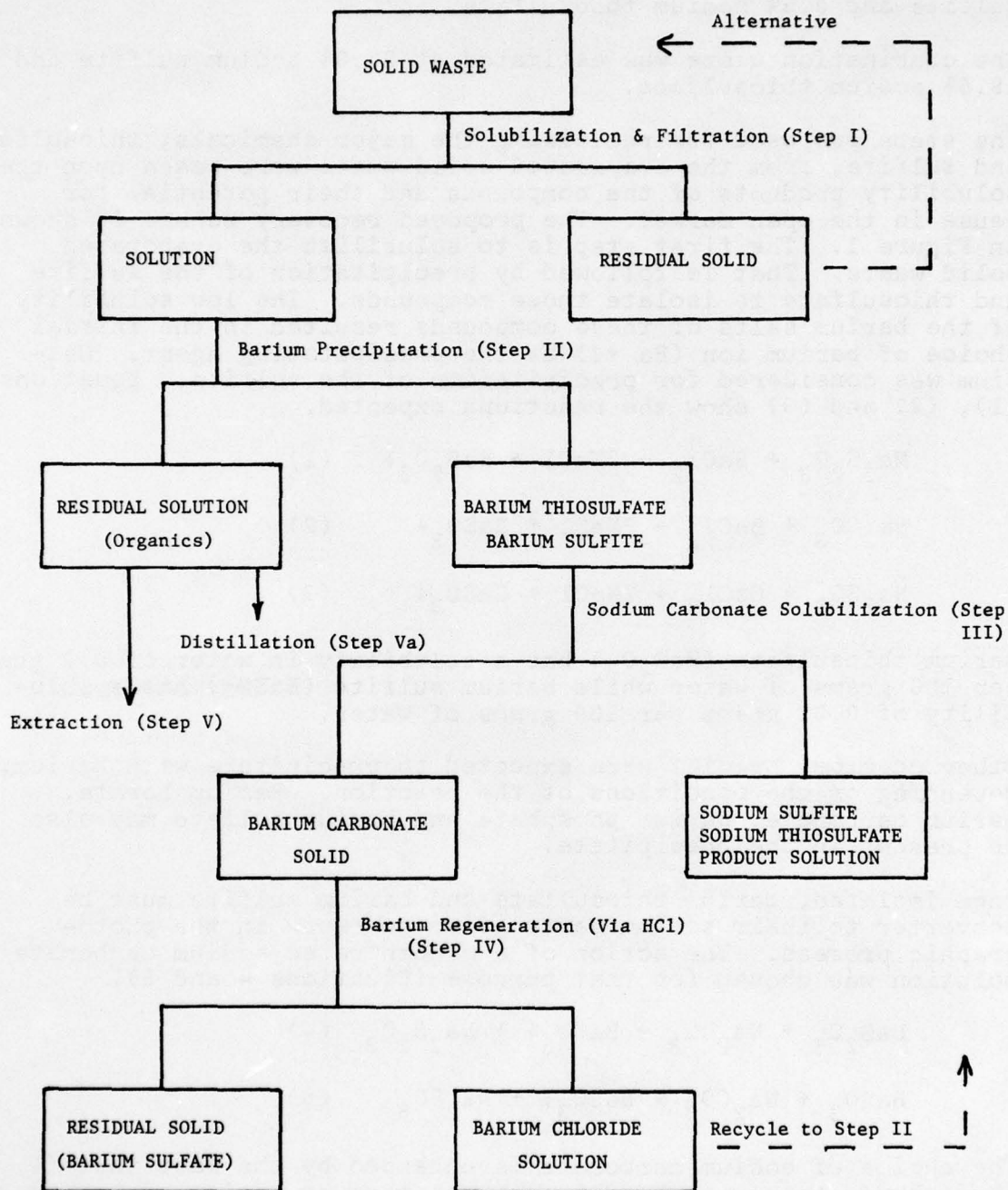
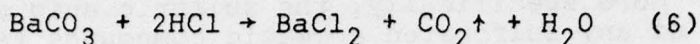


FIGURE 1 - Proposed General Flow Scheme for Recovery of Chemicals from Evaporated, Black-and-White Photographic Processing Wastes

The barium carbonate may then be treated with hydrochloric acid to recover barium for reuse (Equation 6).

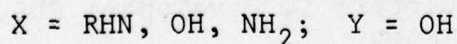
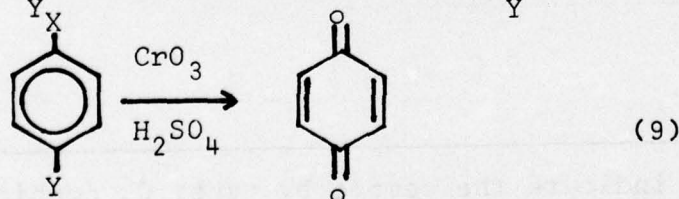
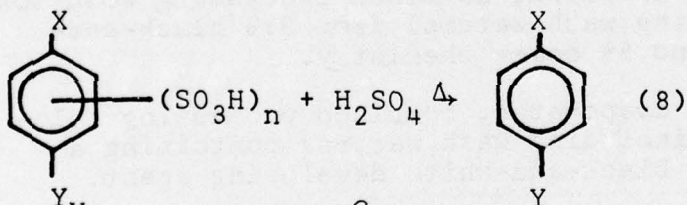
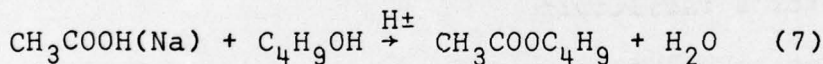


Theoretically, the barium salts of phosphate, borate and carbonate can be removed from the barium sulfite and barium thiosulfate using an acid wash (pH 5-6) to dissolve the former compounds prior to the sodium carbonate addition. Barium phosphate and barium borate might be retained through the sodium carbonate step to be isolated in the barium recycling step.

The organic compounds chosen for recovery include acetic acid, hydroquinone and para-aminophenol. Recovery methods included reclamation by either distillation or solvent extraction at controlled pH. However, the known sulfonation reactions of black-and-white photographic developers (hydroquinone and elon) were expected to cause interferences in the recovery scheme.

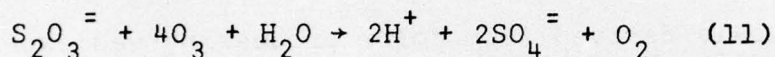
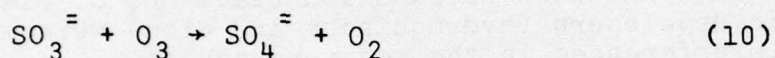
Recovery of chemicals derived from color processing was expected to be accomplished in the following manner: Iron and cyanide (as ferrocyanide or ferricyanide) can be removed by addition of iron salts (such as ferrous sulfate). This gives insoluble iron ferro- or ferricyanide precipitates. The color developers and benzyl alcohol may be isolated by organic solvent extraction from a water solution followed by extraction of the organic layer with dimethylformamide (DMF).

An alternative program proposed to reclaim the organics included conversion into more recoverable materials. Acetic acid (or sodium acetate) can be reacted with butyl alcohol and sulfuric acid (Equation 7) to produce butyl acetate. The latter can be removed by azeotropic distillation.



The resultant solution (after distillation) is then heated with concentrated sulfuric acid followed by addition of chromic anhydride (or potassium dichromate) to effect oxidation of the remaining organics. More specifically, the sulfuric acid step gives desulfonation of any sulfonated aromatic compounds (such as hydroquinone monosulfonate) while the chromic acid oxidizes any para-aminophenol derivatives to quinone. Hydroquinone is also oxidized to quinone under these conditions. (See Equations 8 and 9.)

The quinone may then be isolated by ether extraction. If the organic compounds cannot be isolated, treatment to reduce the Chemical Oxygen Demand (COD) is required. Ozonation is acceptable for that purpose. Ozonation causes precipitation of sodium sulfate from oxidation of sulfite and thiosulfate (Equations 10 and 11).



The reaction requires addition of a caustic to maintain reaction rates.

SECTION II

MATERIALS

Photographic Wastes

Six separate waste samples were received from the Air Force for evaluation at CPAC. These are listed below in order of receipt at the Contractor's facility:¹

Waste C-1 - Used, evaporated, combined processing solutions (including wash waters) from 95% black-and-white and 5% color chemistry.

Waste C-2 - Unused, evaporated, combined processing solutions (including wash waters) containing a viscous black-and-white developing agent.

1. These notations indicate the sample by type: C, combined; F, fix; FD, fix plus developer; D, developer; FDS, fix plus developer and short stop.

- Waste F-1 - Used, evaporated, black-and-white fix.
- Waste FD-1 - Used, evaporated, black-and-white fix and developer mixture.
- Waste D-1 - Used, evaporated, black-and-white developer.
- Waste FDS-1 - Used, evaporated, black-and-white fix, developer and short stop only.

All fix solutions had been desilvered electrolytically prior to evaporation. With the exception of the developer waste (D-1), all samples had been evaporated to a solid. Sample C-2 was not evaluated because the solutions were never used to process a photographic product.

2. Chemicals

The chemicals used in this study were as follows:

- Butanol, Fisher Certified Grade;
- Barium Chloride Dihydrate, Fisher Technical Grade;
- Cocoon Charcoal (activated), Fisher 50-200 Mesh;
- Ethyl Ether (Anhydrous), Fisher Certified Grade;
- Hydrochloric Acid (37%), Fisher Reagent Grade;
- Methanol, Fisher Certified Grade;
- Potassium Dichromate, Fisher Reagent Grade;
- Sodium Carbonate Monohydrate, Fisher Laboratory Grade;
- Sodium Hydroxide, Fisher Certified Grade;
- Sodium Sulfate (Anhydrous), Fisher Laboratory Grade;
- Sulfuric Acid (85-98%), Fisher Reagent Grade;
- Water, Distilled and Stored in Polyethylene Containers.

All chemicals used for analytical measurements were Reagent Grade, as supplied by Fisher Scientific or Eastman Kodak Company.

SECTION III

APPARATUS

Standard laboratory reaction glassware (beakers and round bottom flasks), mixing equipment (magnetic and overhead stirrers), filtration units (Buchner and frit glass funnels, and filtering flasks), and heating equipment (hot plates and heating mantels) were used. A Brinkman Rotavapor-R evaporator was employed for quick solvent removal.

Instruments used include: Perkin-Elmer Model 360 Atomic Absorption Spectrophotometer, a Perkin-Elmer/Coleman Model 139 Visible-Ultraviolet Spectrophotometer, and a Perkin-Elmer Model 137 Infrared Spectrophotometer.

Other auxiliary equipment utilized was a Corning Model 12 Research pH Meter, a Metler H-10 Analytical Balance, a Laboratory Devices Mel-Temp melting point apparatus, and a Will Scientific Lab Oven for drying of solids.

Ozonation studies were done using a high frequency, 4-cell CPAC unit (OZ-60) fed by a Joy Twistair (TA-07T8N2C) air compressor. The reaction column was a vertical plexiglass cylinder (4 ft. by 3 in. diameter) containing a gas sparger sealed into the bottom.

SECTION IV

PROCEDURE

1. Analysis of Evaporated Solid Waste Samples

Each waste sample (except C-2) was analyzed for the major constituents as required. The analytical procedures used were those obtained from the following references:

- 1) The Eastman Kodak Manual for Control of Black-and-White Processing Chemistry,²
- 2) the ANSI Standards on Photographic Processing Effluents³, and
- 3) The 13th Edition of Standard Methods for Water and Wastewater Analysis⁴.

-
2. Chemical Control Procedures for Black-and-White Film Processing, March 1966, Motion Picture and Education Markets Div., Eastman Kodak Co., Rochester, N.Y. 14650.
 3. American National Standard on Photographic Processing Effluents, PH4.37-1975, April 2, 1975, American National Standards Institutes, Inc., 1430 Broadway, New York, N.Y. 10018.
 4. Standard Methods for the Examination of Water and Wastewater, 13th Ed., 1971, American Public Health Assoc., 1015 18th St., N.W., Washington, D.C.

2. General Procedure for Evaluating Proposed Recovery Scheme

The general steps required to evaluate the proposed flow scheme include:

- 1) Grinding the sample.
- 2) Dissolving the sample in a solvent.
- 3) Filtration to remove insoluble residue.
- 4) Analysis of inorganics in solution.
- 5) Addition of barium salts (conditions: at 80°C, 10-20% excess of BaCl₂, no pH adjustment, mixing 4 hours).
- 6) Filtration to remove barium salts of thiosulfate and sulfite.
- 7) Analysis of remaining thiosulfate and sulfite in solution.
- 8) Addition of sodium carbonate solution to solid (conditions: 10-20% excess, at 25-50°C, no pH adjustment, mixing 24 hours).
- 9) Filtration to remove barium carbonate precipitate.
- 10) Analyze solution for thiosulfate and sulfite.
- 11) Addition of hydrochloric acid to barium carbonate precipitate.
- 12) Filter barium chloride solution for reuse.
- 13) Treatment of initial solution (7 above) for recovery of organics.
- 14) Calculation of recovery efficiencies and product purity.
- 15) Photographic testing of isolated chemicals.
- 16) Cost analysis.

Much of the procedure had been tested previously at CPAC using barium to precipitate the sulfur salts with some success.

Major modifications of the proposed scheme for handling the organic portion of the waste became necessary as work continued.

The evaporated wastes received were hard, but brittle. The waste was chipped into small portions for handling. Those fragments were then ground to coarse granularity to enhance dissolution in a reasonable time.

Various approaches to isolating thiosulfate and sulfite within the framework of the proposed scheme were investigated. Each was directed at increasing yields, separation, or purity of thiosulfate and sulfite.

The dissolution step was directed at putting the solid into solution in a small volume rapidly. The solvent choices included hydrochloric acid, sodium hydroxide, ammonium hydroxide, methanol and water. Each was investigated by measuring the amount of insoluble products remaining after addition of the evaporated solid. This was done at various ratios of solid to solution. The amount of important compounds (primarily thiosulfate and sulfite) in each phase was then determined. The selected solvent would have most of these components in either the remaining solid or the solution. Emphasis was placed on putting all sulfite and thiosulfate into solution.

The next step was to isolate the inorganic salts of sulfite and thiosulfate. Barium salts of these compounds are insoluble. The calcium salt of sulfite is insoluble, while the calcium salt of thiosulfate is quite soluble. Various amounts of each ion were added in quantities from that stoichiometrically required for complete removal to a 50% excess. This step produces a solution containing unprecipitated organics (and certain inorganics) and solid compounds of thiosulfate and sulfite.

The solid compounds were treated to recover both the metal for recycle and the sulfur salts. Various quantities of sodium carbonate were added and conversion to insoluble metal carbonates measured. The success of the schemes required maximum recovery of the metal for reuse due to the potential pollution characteristics of metal ions. Sodium carbonate was added at fractions of 1.0, 1.1, 1.3 and 1.5 times that stoichiometrically required by the calcium or barium present. Yields of sodium thiosulfate and sodium sulfite were measured and recorded. These studies were carried out at various temperatures for different reaction times. The temperature was varied from 25° to 90°C and reaction times from one to ten hours for the precipitation step. The sodium carbonate step was conducted at 25-50°C and reaction times of 1-40 hours. The pH was not adjusted, but was always above pH 7, except for the metal ion recycling step.

The residual solution was treated with certain solvents to recover substantial benzene compounds (i.e. hydroquinone, elon) including sulfonated fractions of each, or reacted in situ with other chemicals followed by solvent extraction or distillation of the reaction product.

The solid metal carbonate was reacted with hydrochloric acid for recovery of the barium or calcium as the chloride salt. The acid was added in excess of that required by the amount of metal present. Temperature was allowed to change according to the exothermic heat of solution. Thiosulfate and sulfite, as recovered by the proposed flow scheme, were tested photographically at Wright-Patterson Air Force Base. The procedure used is shown in Appendix B.

Ozone oxidation studies on residual solutions to remove COD were performed. A 3 gram/hour unit ozonator supplied ozone in an air stream to a 3-inch oxidation column. Removal of COD was measured without regard to efficiency of ozone usage.

Cost studies were performed using product yields and the latest commercial bulk prices.

3. Procedures for Treatment of Individual Evaporated Solid Wastes

Table 2 lists the specific procedures as applied to each of the solid waste samples received. Such specific procedure modifications were required due to the absence of certain recoverable compounds in the samples received. Step numbers refer to the proposed recovery scheme (Figure 1). Each is detailed as follows:

a. Solvents used to Redissolve Evaporated Solid:

Water was evaluated for the initial dissolution of the solid for all samples. Sodium hydroxide was used on all samples except F-1. Methanol was only used on D-1, while hydrochloric acid and ammonium hydroxide were used only on samples C-1.

b. Recrystallization of Salts Prior to Precipitation:

Thiosulfate and sulfite may crystallize from the Step 1 concentrated solutions upon cooling. This cooling step was evaluated on all samples.

Crystallization was evaluated by first allowing the samples to cool to room temperatures and observing crystallization. A further evaluation was carried out by cooling to 5°C for 24 hours. Crystals were then isolated by filtration and product yields determined after drying. Crystals isolated in this manner were air dried at 25-35°C for sodium thiosulfate pentahydrate, and 150°C for sodium sulfite.

Selected samples were sent to Wright-Patterson Air Force Base for evaluation in a photographic process.

c. Precipitation of Thiosulfate and Sulfite (Step II):

Two precipitating agents were employed for isolating thiosulfate and sulfite from solution. Barium ion (Ba^{+2}) was evaluated on all waste samples. Calcium ion (Ca^{+2}) was evaluated as an alternative method of separating thiosulfate from sulfite by selective precipitation of calcium sulfite. Following filtration of the latter, barium was used to precipitate the thiosulfate.

d. Ether Extraction of Residual Solutions After Thiosulfate and Sulfite Precipitation (Step V):

Ether extraction of residual solutions containing most of the organics from the combined waste (C-1) and the developer waste (D-1) were conducted at both pH 8 and pH 5 to extract elon (para-methylaminophenol) and hydroquinone.

An alternative procedure involving desulfonation and oxidation prior to ether extraction was attempted on the same wastes. Concentrated sulfuric acid was added to the residual solutions (20% of the solution by volume), and the solution refluxed for two hours while steam was passed into the solution from an external source. After cooling of the solution, potassium dichromate (large excess) in concentrated sulfuric acid was added and the mixture allowed to reflux for 2-4 hours. Ether extraction was then expected to isolate quinone from the water solution. Experimental work on desulfonation and oxidation reactions was limited.

TABLE 2
VARIATIONS IN THE GENERAL PROCEDURE
FOR INDIVIDUAL EVAPORATED WASTES

<u>Specific Procedure</u>		<u>C-1</u>	<u>F-1</u>	<u>FD-1</u>	<u>D-1</u>	<u>FDS-1</u>	<u>Comments</u>
Step I	HCl	Yes	No	No	No	No	
	H ₂ O	Yes	Yes	Yes	Yes	Yes	
Solvents used to	NH ₄ OH	Yes	No	No	No	No	
Redissolve Solid:	NaOH	Yes	No	Yes	No	Yes	
	Methanol	No	No	No	Yes	No	
Test for Recrystallization of Salts upon Cooling		Yes	Yes	Yes	Yes	Yes	D-1 for sulfite only
Step II							
Chemicals Tested to Precipitate Thiosulfate and Sulfite:	Barium	Yes	Yes	Yes	Yes	Yes	D-1 for sulfite only
	Calcium	Yes	No	Yes	No	No	
Step V							
Ether Extraction of Residual Solu- tion After Thio- sulfate & Sulfite Precipitation:	Without Preoxida- tion	Yes	No	No	Yes	No	
	With Pre- oxidation	Yes	No	No	Yes	No	
Step Va							
Distillation Isolation of Butyl Acetate		Yes	No	No	Yes	No	

e. Distillation Isolation of Butyl Acetate (Step Va):

Recovery of acetic acid (or sodium acetate) was attempted by refluxing the residual solution with n-butyl alcohol (excess) and sulfuric acid (0.1% or The solution volume) for 2 hours followed by distillation of the three component azeotrope (butyl alcohol, butyl acetate and water, b. p. 90.7°C). The upper layer is expected to contain mostly butyl acetate while the lower layer can be recycled to the reaction pot.

SECTION V

RESULTS

1. Analysis of Evaporated Solid Waste Samples

Analysis of the waste received are shown in Table 3.

TABLE 3

ANALYSIS OF EVAPORATED PHOTOGRAPHIC WASTE SAMPLES

Compounds	Waste Material (% of Dry Weight) ^(a)				
	Combined (C-1)	Fix (F-1)	Fix & Developer (FD-1)	Developer (D-1)	Fix + Dev. + Short Stop (FDS-1)
Sodium Sulfite (Na_2SO_3)	13.6	7.3	9.8	16.7	22-28
Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$)	40.5	58.8	56.9	N.D.	19-50
Boron (as B)	1.0	0.07	0.5	2.1	0.6
Phosphate (as $\text{PO}_4^{=}$)	0.06	--	0.06	0.1	0.16
Sulfate ^(b) (as $\text{SO}_4^{=}$)	30.6	N.D.	2.0	N.D.	N.D.
<u>para</u> -n-Methyaminophenol (Elon)	0.15	--	0.3	N.D.	0.04
Hydroquinone (HQ)	0.06	--	0.02	N.D.	0.04
Sodium Hydroquinone Monosulfonate (HQS) ^(c)	3.3	--	0.6	43.6	5.2
Silver (Ag)	0.1	1.0	--	--	--
Iron (Fe)	0.04	--	--	--	--
Cadmium (Cd)	<u>0.001</u>	<u>--</u>	<u>--</u>	<u>--</u>	<u>--</u>
	89.411	67.17	70.18	62.5	60.44

N.D. - Not Detected

-- - Not Determined

TABLE 3

(Cont.)

ANALYSIS OF EVAPORATED PHOTOGRAPHIC WASTE SAMPLES

- a) - Water present in each sample was determined by the weight loss accompanying drying at 110°C for 24 hours. Water content found for each was: C-1, 20%; F-1, 31.5%; FD-1, 19.5%; D-1, 25%; FDS-1, 20.5%.
- b) - Determined gravimetrically (as barium sulfate) taking into account the inference by thiosulfate and sulfite.
- c) - Includes a variety of sulfonates determined as hydroquinone monosulfonate.

All wastes, except the developer waste, have 50-66% of the total dry weight as sodium sulfite plus sodium thiosulfate. The sodium thiosulfate concentration ranges from 29-59%. Table 4 shows the range of ratios of sodium thiosulfate to sodium sulfite found for samples received.

TABLE 4

WEIGHT RATIO OF SODIUM THIOSULFATE TO
SODIUM SULFITE PRESENT IN WASTE SAMPLES

<u>Waste Sample</u>	<u>Designation</u>	<u>Weight Ratio</u> <u>$\text{Na}_2\text{S}_2\text{O}_3:\text{Na}_2\text{SO}_3$</u>
Combined	C-1	3:1
Fix	F-1	8:1
Fix + Developer	FD-1	5.8:1
Developer	D-1	---
Fix + Developer + Short Stop	FDS-1	1:1 to 2.3:1

The last waste received (FDS-1) was not homogeneous. Thus, various areas of the 15-pound sample showed different analyses for sodium thiosulfate and sodium sulfite. The range of ratios was between 1:1 and 2.3:1 as shown in Table 4.

The residual water content of the evaporated solids ranged from 19.5% to 31.5% of the total weight. Water content affects the solubility characteristics of the waste. In general, the evaporated waste samples are 97-99% soluble in water.

In all cases, only trace amounts (1.04-0.3%) of elon and hydroquinone were found (Table 3). These compounds are probably decomposed during the evaporation step.

Hydroquinone monosulfonate (HQS), a by-product of the photographic process was found in each waste, except for sample FD-1; fix plus developer. The large value for HQS in the developer waste is not surprising, since it represents contributions from the monosulfonates and disulfonates of both elon and hydroquinone.⁶

Silver, iron, cadmium, boron and phosphate are generally present in very low concentrations. Sulfate is not easily determined when sulfite, thiosulfate, phosphate and borate are present. No sulfate was found by analysis in three of the wastes. Sulfate is produced by aerial oxidation of both sulfite and thiosulfate. Therefore, the absence of sulfate places doubt on the analytical method. Further work on an analytical method for sulfate in the presence of sulfite and thiosulfate was not justified.

The analytical results shown in Table 3 confirm that thiosulfate and sulfite represent the major portion of the evaporated solid. Most of the contract work was thus directed at these compounds.

Boron, phosphorous and metals are present at such low concentrations that efforts at recovery were not considered.

The organics selected initially for recycle (elon, hydroquinone, and acetic acid) are also present at levels below that considered acceptable for direct recovery. Therefore, a re-evaluation of the recovery of the organic compounds was made. It was determined that attempts to recover the sulfonated portions of the two developing agents was practical. Thus, some work was directed at these compounds. However, that work was given secondary priority.

2. Solubilization of Solid Waste Samples

Each waste will be discussed separately with special attention given to reasons why the originally proposed scheme required modification.

In all cases, solubilization involved using the solvent in ratio to the evaporated solid from 1:1 to 0.5:1 by weight.

6) Private communications with Dr. C. Bard, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.

It was found that if the sodium thiosulfate concentration is below approximately 50% of the total dry weight and the ratio of thiosulfate to sulfite is less than or equal to 3:1, water solubilization of the waste does not allow crystallization of the sodium thiosulfate pentahydrate upon cooling. Yields of thiosulfate and sulfite recovered and the volume of solution required using water solubilization make direct barium precipitation of the total water solution impractical. Thus, an alternative method was sought. The use of concentrated sodium hydroxide solution as the solubilizing agent separated thiosulfate from sulfite with satisfactory results. Ammonium hydroxide also worked well, but the ammonia vapors constitute a hazard. With sodium hydroxide, materials handling is more practical and higher yields are realized. Hydrochloric acid was considered impractical because thiosulfate and sulfite decomposed under solubilization.

If the amount of sodium thiosulfate in the waste is greater than 50% of the dry weight and the ratio of thiosulfate to sulfite is greater than 3:1, water solubilization followed by crystallization of sodium thiosulfate pentahydrate works best. That results in less barium usage and lower solution volumes to be handled.

3. Application of General Flow Scheme to Specific Evaporated Wastes

a. Simulated Wastes:

Tests using laboratory grade chemicals showed that when sodium thiosulfate and sodium sulfite are reacted with barium chloride individually, yields of 85-95% of the barium salts are realized under the following conditions:

- 1) Reaction Temperature, 70-80°C.
- 2) Reaction time, >3 hours.
- 3) pH >7.

If the sodium thiosulfate and sodium sulfite are reacted in the same vessel with barium chloride under these conditions, longer reaction times are required.

The sodium carbonate dissolution reaction is much faster for barium thiosulfate than barium sulfite. Increased reaction times result in only 50% recovery of sulfite, but

nearly 100% recovery of thiosulfate. Optimum sodium carbonate conditions include mixing at 25-50°C for 24 hours. That balances the effects of aerial oxidation of newly formed sulfite due to stirring and the necessary contact time for the resolubilization reaction to take place.

b. Combined Waste (C-1):

The combined solution photographic wastes (C-1) was the first sample received. It was given considerable attention because it allows the maximum flexibility at the evaporation site. This waste contained 40.5% sodium thiosulfate and 13.6% sodium sulfite ($\text{Na}_2\text{S}_2\text{O}_3:\text{Na}_2\text{SO}_3$ approximately 3:1). It was found that the best solubilizing agent was sodium hydroxide as opposed to water as discussed earlier. It was necessary to modify the general scheme for recovery as shown in Figure 2. The results are thus not applied to this modified general scheme. Results are shown in Table 5.

The ground waste (A) was mixed with 40% sodium hydroxide (Step 1). The resulting thiosulfate solution (B) contains approximately 80-90% of the available thiosulfate but only 5-10% of the available sulfite. The remaining solid (C) contains 90-95% of the sulfite and 10-20% of the thiosulfate. The thiosulfate solution (B) was reacted at 70-80°C with a barium chloride solution (Step 2) to precipitate the barium thiosulfate and barium sulfite (Solid D); removed by filtration. The resulting solution (E) contains the organics and small quantities of unreacted sulfite and thiosulfate. Thiosulfate removal is about 90% effective in this step. The barium salts (C) were then mixed at 25-50°C with a sodium carbonate solution (Step III). This results in a barium carbonate-barium sulfate solid (G) and a thiosulfate solution (F). The carbonate reaction is approximately 70-80% successful in recovering thiosulfate. A small amount of sulfite is carried through to solution (F). That solution was basic due to the presence of unreacted sodium carbonate ($\text{pH}\approx 10$).

The overall yield of thiosulfate is 50-60% of that available. The sulfite isolation procedure is the major modification to the general scheme. Solid (C) measured approximately 40% of the original waste solid; 2% of that solid remaining insoluble upon dissolving it in water. That residue (I) was filtered (Step VI). The barium precipitation procedure was applied to this solution (Step VII). The resulting precipitate (J) analyzed to contain 85-90%

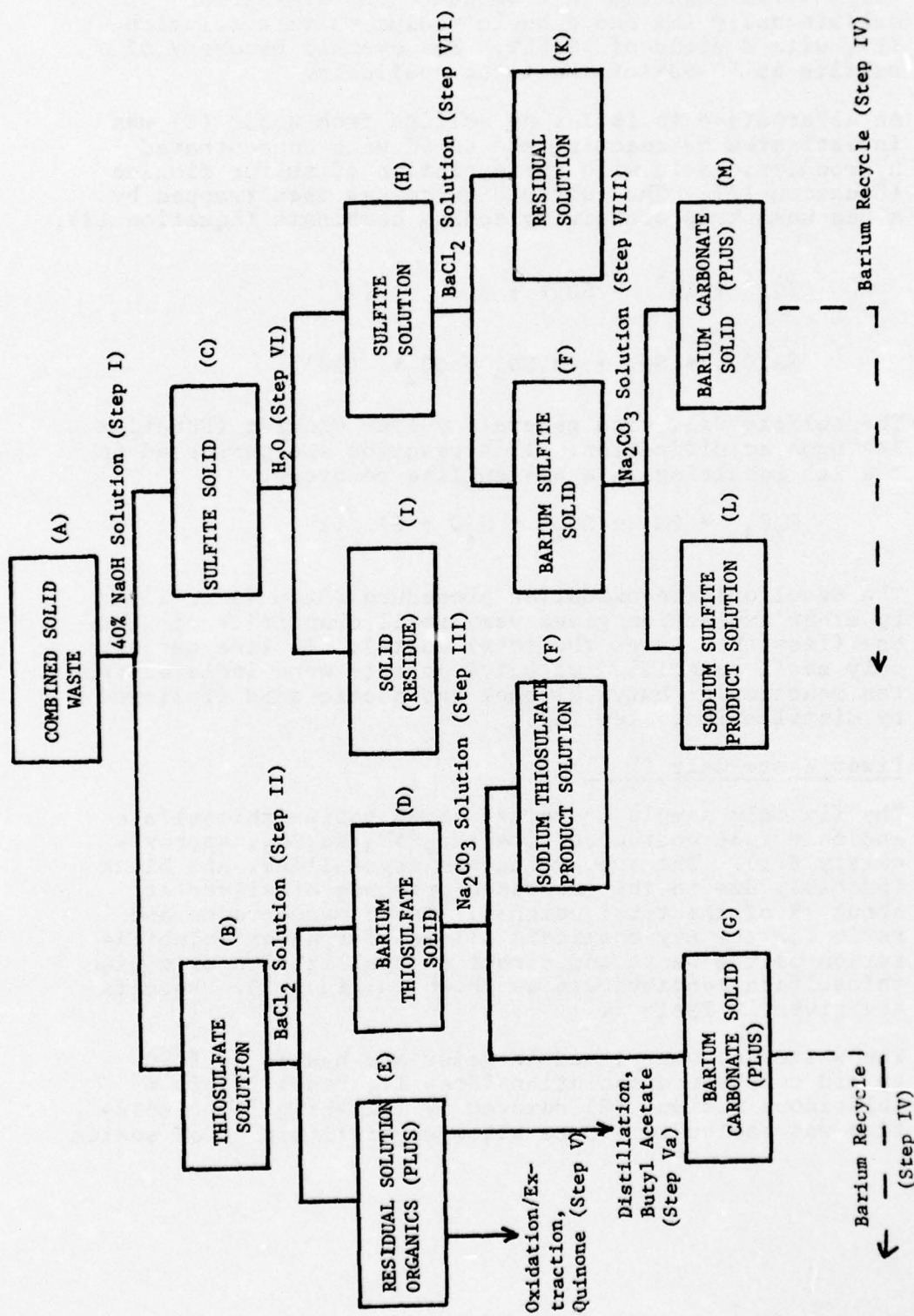
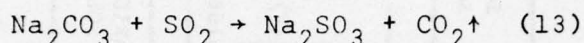
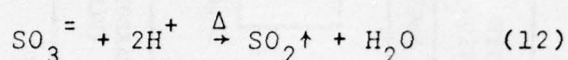


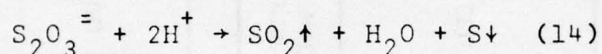
FIGURE 2 - Flow Scheme for Recovery of Chemicals from Combined Photographic Wastes

of the available sulfite. Sodium carbonate treatment (Step VIII) resulted in a barium carbonate-barium sulfate solid (M) and a basic sodium sulfite solution (L), with a yield of 75-85%. The overall recovery of sulfite is 50-60% of the total available.

An alternative to isolating sulfite from solid (C) was investigated by reacting the solid with concentrated hydrochloric acid with the evolution of sulfur dioxide (Equation 12). The sulfur dioxide was then trapped by a gas wash trap containing sodium carbonate (Equation 13).



Thiosulfate will also generate sulfur dioxide (Equation 14) upon acidification. This reaction was performed in the lab resulting in a 91% sulfite recovery.



The desulfonation-oxidation procedure (Step V) followed by ether extraction gives very small quantities of quinone (less than 1% of the total waste). In like manner, only small quantities of butyl acetate were isolated from the reaction of butyl alcohol and acetic acid (followed by distillation, Step Va).

c. Fixer Waste Only (F-1):

The fix only sample contained 58.8% sodium thiosulfate and only 7.3% sodium sulfite ($\text{Na}_2\text{S}_2\text{O}_3/\text{Na}_2\text{SO}_3$, approximately 8:1). The appearance was crystalline, and black (probably due to the increased presence of silver at about 1% of the total weight). These percentages and ratio for the key chemicals allowed for water solubilization of the waste and direct crystallization of sodium thiosulfate pentahydrate as shown in Figure 3. Results are given in Table 5.

The waste (A) was placed in water and heated to 80°C to aid complete dissolution (Step I), resulting in a gelatinous residue (C) removed by filtering. The solution was cooled to 5°C to allow crystallization of sodium

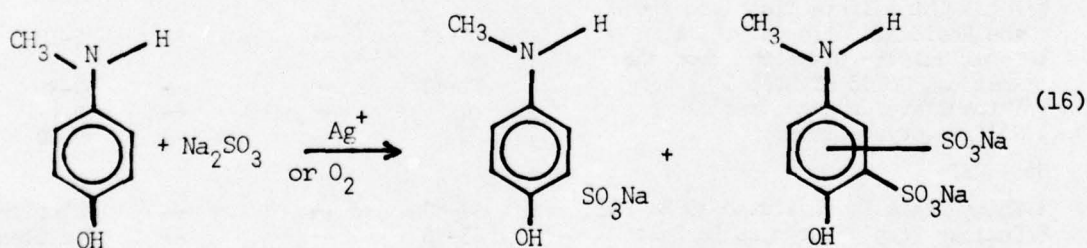
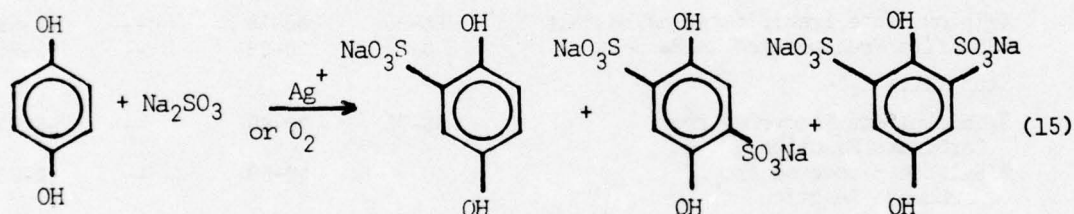
TABLE 5
THIOSULFATE-SULFITE YIELDS DURING RECOVERY

	- W A S T E S -			
	<u>C-1</u>	<u>F-1 & FD-1</u>	<u>D-1</u>	<u>FDS-1</u>
Initial Concentration:				
%/Thiosulfate of Total Waste	40	56-59	0	29-50
%/Sulfite of Total Waste	14	7-10	17	22-28
Type of Solubilization in Step I	Base	Water	Water	Base
Step I:				
%/Total Thiosulfate Dissolved	80-90	80-90	--	70-80
%/Total Sulfite Dissolved	5-10	30-40	90-95	5-10
%/Thiosulfate Crystallized	0	30-50	--	0
%/Sulfite Crystallized	0	0	40-60	0
Step II:				
%/Thiosulfate Precipitated as Ba Salt	85-95	90-98	--	45-55
%/Sulfite Precipitated as Ba Salt	0	90-98	--	85-95
Step III:				
%/Thiosulfate Recovered from Carbonate Reaction	65-75	70-80	--	85-90
%/Sulfite Recovered from Carbonate Reaction	0	40-50	--	50-60
Step VI:				
%/Total Thiosulfate Dissolved from the Residual Solid of Step I	5-10	--	--	5-10
%/Total Sulfite Dissolved from the Residual Solid of Step I	70-80	--	--	90-95
%/Thiosulfate Crystallized	0	--	--	0
%/Sulfite Crystallized	0	--	--	40-50
Step VII:				
%/Thiosulfate Precipitated as Ba Salt	30-40	--	--	Solution
%/Sulfite Precipitated as Ba Salt	85-95	--	--	Recycled
Step VIII:				
%/Thiosulfate Recovered from Carbonate Reaction	45-55	--	--	to
%/Sulfite Recovered from Carbonate Reaction	75-85	--	--	Step II
Total Yield:				
%/Thiosulfate Recovered	50-60	60-90	--	35-50
%/Sulfite Recovered	50-60	10-20	35-55	45-55

thiosulfate pentahydrate (D). About 40-50% of the thiosulfate was removed by that procedure. The remaining thiosulfate-sulfite solution (B) was reacted with barium chloride solution at 70-80°C (Step II). The solid (E) was reacted with sodium carbonate solution (Step III) resulting in a barium carbonate solid (F) and a sodium thiosulfate-sodium sulfite basic solution (G). The barium chloride-sodium carbonate process is 70-80% effective for thiosulfate and about 40-50% effective for sulfite. Overall, recovery for thiosulfate is 60-80% of the total available and 10-20% for sulfite.

d. Developer Waste (D-1):

The developer only sample contained 16.7% sodium sulfite, but very little of the organics originally anticipated (see Table 3). It is probable that hydroquinone and elon had formed their respective disulfonates under evaporation. The structure of these probable compounds are given in Equations 15 and 16.



These compounds further oxidize to give polymeric materials similar to humic acids (from hydroquinone) and nitrogenous humic acids (from elon), or a combination of both.^{6,9}

9) C.E.K. Mees, *The Theory of the Photographic Process*, The McMillan Company, N.Y., N.Y. 1954, pp. 560-569.

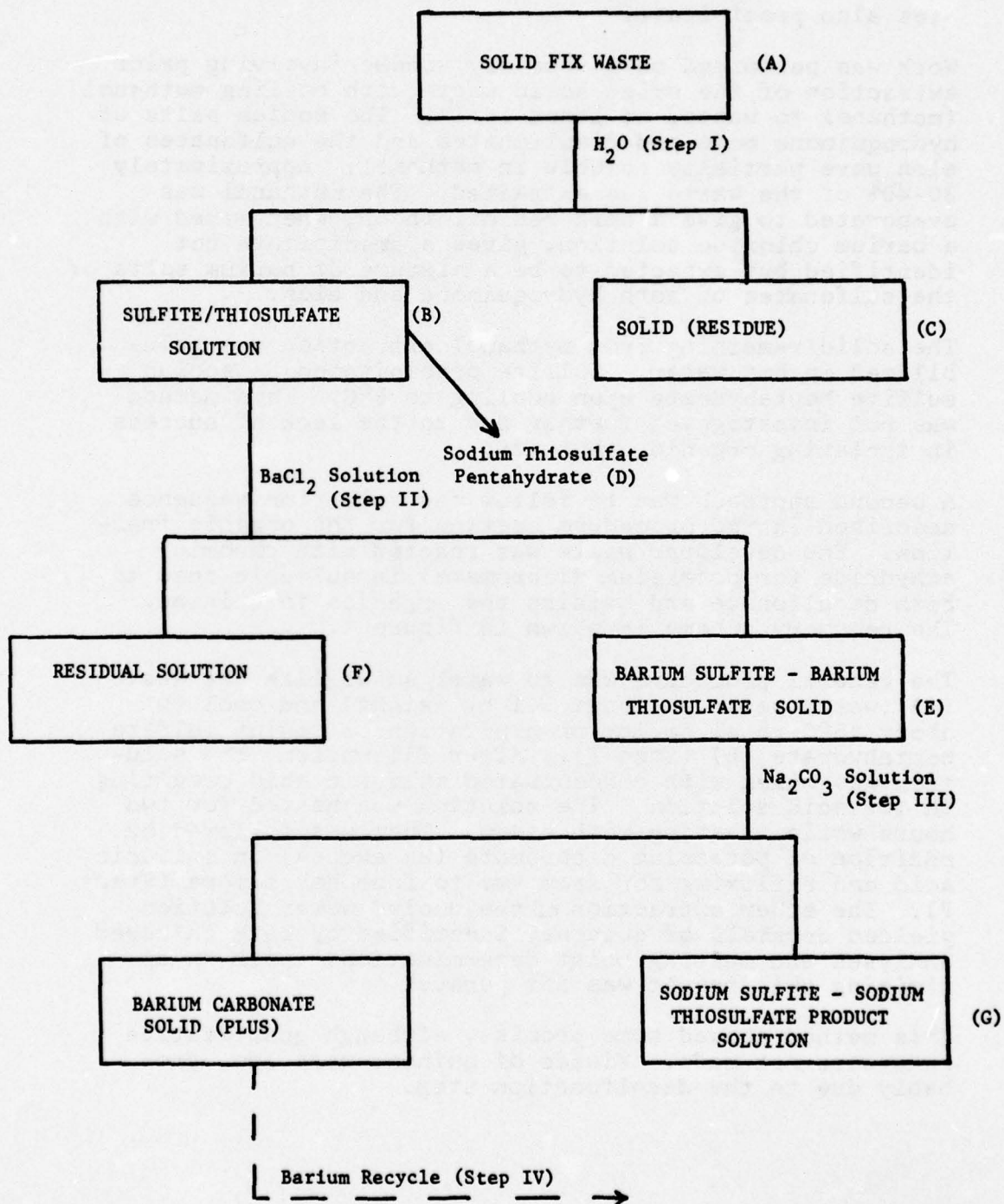


FIGURE 3 - Flow Scheme for Recovery of Chemicals from Evaporated Fixer Waste

Because of this complex composition, alternative approaches were evaluated. The sulfite was removed easily by water solubilization followed by direct crystallization upon cooling. Barium precipitation of the sulfite was tested and found inadequate because the organic sulfonates also precipitate.

Work was performed on a recovery scheme involving prior extraction of the dried solid waste with boiling methanol (methanol to waste, at least 10:1). The sodium salts of hydroquinone mono- and disulfonates and the sulfonates of elon were partially soluble in methanol. Approximately 30-40% of the waste was extracted. The methanol was evaporated to give a dark red oil which, when mixed with a barium chloride solution, gives a precipitate not identified but expected to be a mixture of barium salts of the sulfonates of both hydroquinone and elon.

The solid remaining from methanol extraction was solubilized in hot water. Sulfite precipitated as sodium sulfite heptahydrate upon cooling to 5°C. This method was not investigated further due to the lack of success in isolating organic compounds.

A second approach was to follow the oxidation sequence described in the procedure section for the organic fraction. The developer waste was reacted with chromic anhydride (or potassium dichromate) in sulfuric acid to both desulfonate and oxidize the organics to quinone. The recovery scheme is shown in Figure 4.

The general procedure was to water solubilize the waste (A) (waste:water at least 1:1 by weight) and cool to about ~5°C to allow for precipitation of sodium sulfite heptahydrate (D) (Step I). After filtration, the solution was mixed with concentrated sulfuric acid resulting in 10% acid solution. The solution was heated for two hours while treating with steam. That was followed by addition of potassium dichromate (an excess) in sulfuric acid and refluxing for from two to four hours more (Step V). The ether extraction of the cooled water solution yielded crystals of quinone, identified by both infrared analyses and melting point determination. Work on optimizing this result was not pursued.

This method showed some promise, although quantitative runs were not made. Yields of quinone were low, probably due to the desulfonation step.

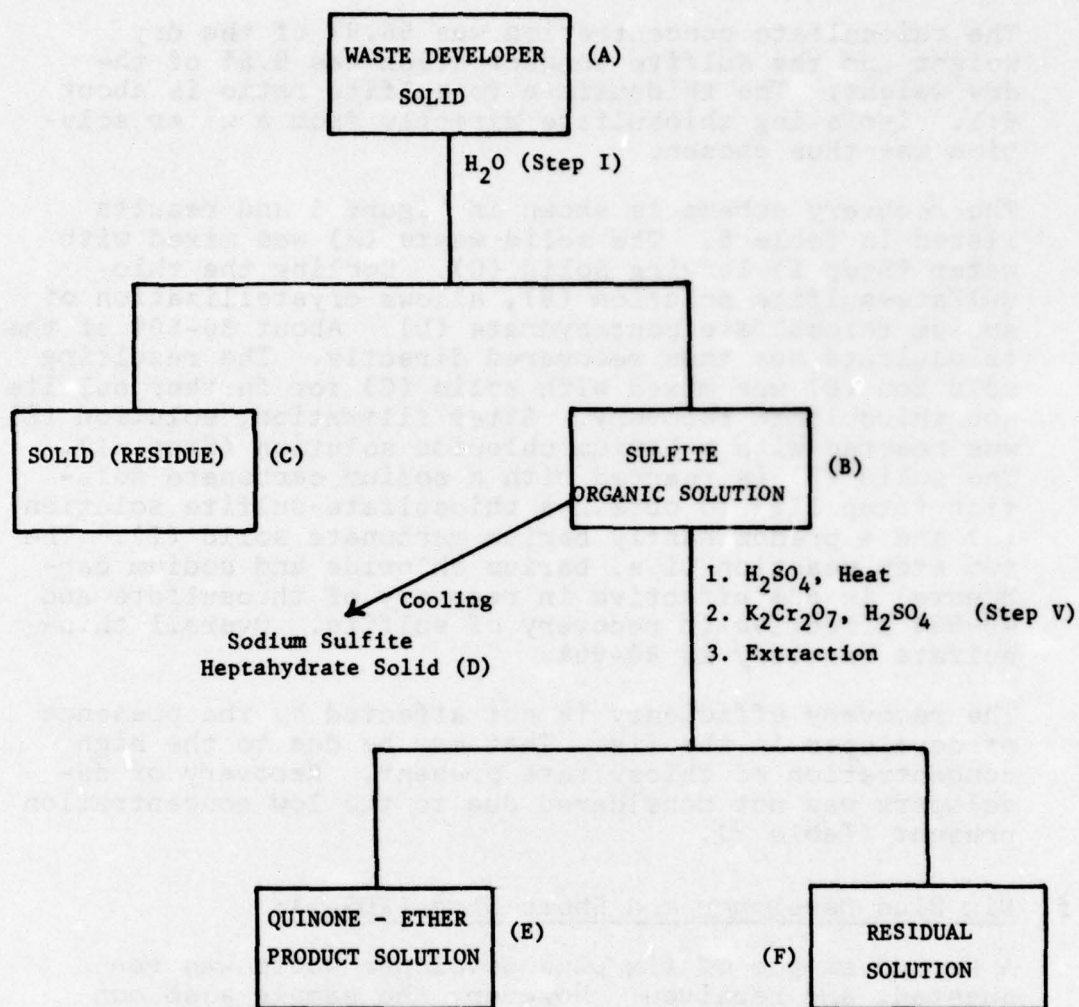


FIGURE 4 - Flow Scheme for Recovery of Chemicals from Developer Waste

As in the combined waste (C-1) very minute amounts of butyl acetate were produced when butyl alcohol and sulfuric acid reacted with Solution (F).

e. Fix Plus Developer Only Waste (FD-1):

The thiosulfate concentration was 56.9% of the dry weight and the sulfite concentration was 9.8% of the dry weight. The thiosulfate to sulfite ratio is about 6:1. Isolating thiosulfate directly from a water solution was thus chosen.

The recovery scheme is shown in Figure 5 and results listed in Table 5. The solid waste (A) was mixed with water (Step I) leaving Solid (C). Cooling the thiosulfate-sulfite solution (B), allows crystallization of sodium thiosulfate pentahydrate (D). About 30-50% of the thiosulfate was thus recovered directly. The resulting solution (E) was mixed with solid (C) for further sulfite and thiosulfate recovery. After filtration, solution (E) was reacted with a barium chloride solution (Step II). The solid (F) is reacted with a sodium carbonate solution (Step III) to obtain a thiosulfate-sulfite solution (H) and a predominantly barium carbonate solid (I). The two step reaction (i.e. barium chloride and sodium carbonate) is 80% effective in recovery of thiosulfate and 40-50% effective in recovery of sulfite. Overall thiosulfate recovery is 80-90%.

The recovery efficiency is not affected by the presence of developer in the fix. That may be due to the high concentration of thiosulfate present. Recovery of developers was not considered due to the low concentration present (Table 3).

f. Fix Plus Developer and Short Stop (FDS-1):

A second sample of fix plus developer waste was requested, and received. However, the sample also contained a short stop bath. The concentration of thiosulfate was thus lower. Unexpectedly, the concentration of sulfite was much higher (18-22%) than the previous samples (Tables 3 and 4). However, the waste was not homogeneous. Analysis of various samples of the same solid showed a range of between 29% and 50% thiosulfate depending upon location of the sample taken for analysis. Most samples contained between 35% and 45% thiosulfate.

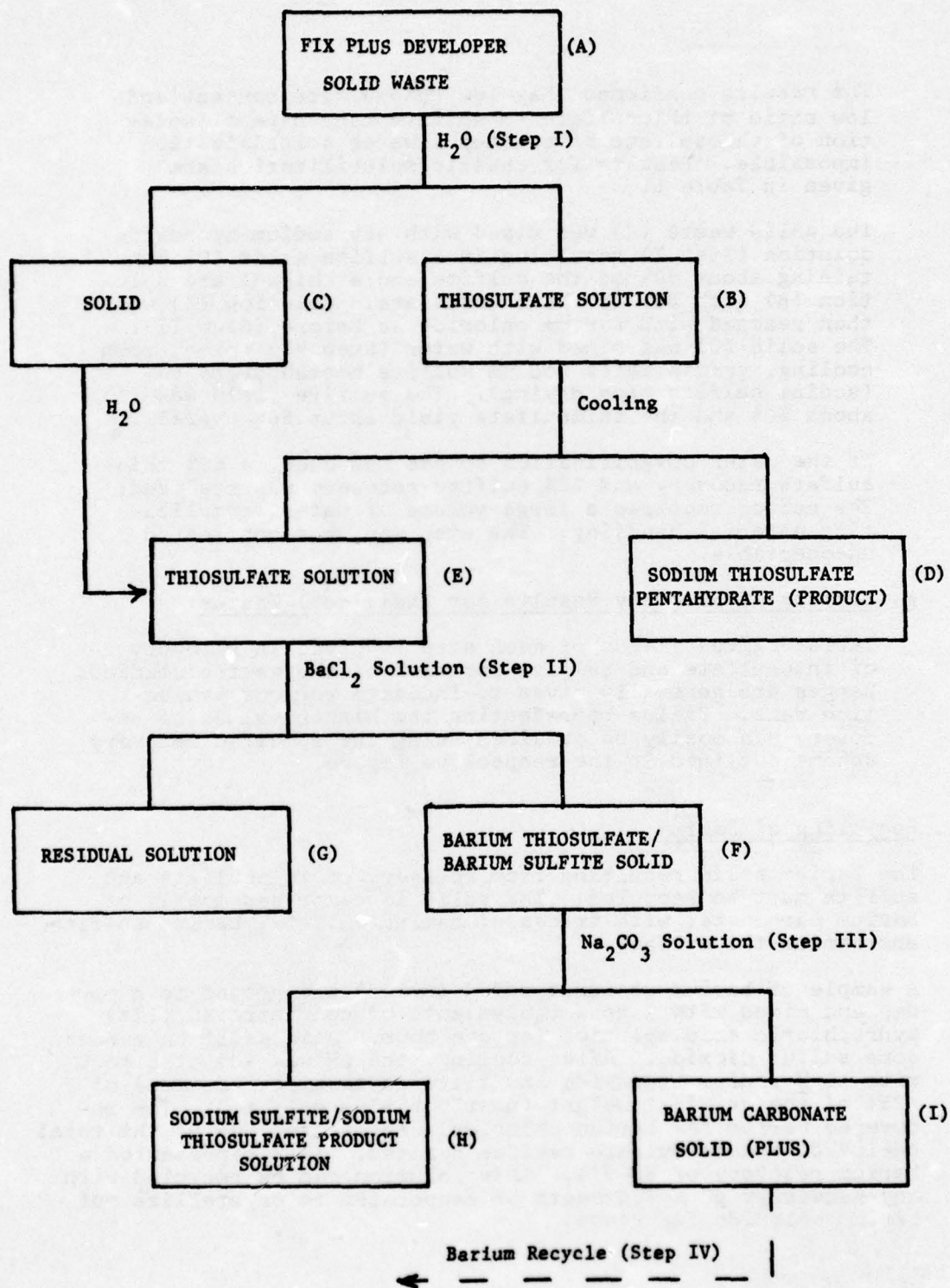


FIGURE 5 - Flow Scheme for Recovery of Chemicals from Fix Plus Developer Waste

The results confirmed that low thiosulfate content and low ratio of thiosulfate to sulfite made direct isolation of thiosulfate after Step I water solubilization impossible. Results for caustic solubilization are given in Table 5.

The solid waste (A) was mixed with 40% sodium hydroxide solution (Step I) resulting in a sulfite solid (C) containing about 90% of the sulfite and a thiosulfate solution (B) with 80% of the thiosulfate. Solution (B) was then reacted with barium chloride as before (Step II). The solid (C) was mixed with water (Step VI) which, upon cooling, precipitates sodium sulfite heptahydrate (J) (sodium sulfite upon drying). The sulfite yield was about 50% and the thiosulfate yield about 50% overall.

If the water solubilization scheme was used, a 60% thiosulfate recovery and 20% sulfite recovery was realized. The method requires a large volume of water, complicating material handling. The step was thus considered unacceptable.

g. Summary of Recovery Results for Individual Wastes:

Table 5 gives yields of each step involved in recovery of thiosulfate and sulfite for each of the wastes studied. Ranges are generally given to indicate various evaluation runs. Yields representing the higher values of recovery can easily be obtained using the specific recovery scheme outlined in the respective figure.

4. Recycling of Barium

The barium solid resulting from recovery of thiosulfate and sulfite must be recycled. The solid is comprised mostly of barium carbonate, with traces of barium sulfate, barium sulfite and barium thiosulfate.

A sample of barium residual solid (dried) was ground to a powder and mixed with 1 to 2 equivalents of concentrated (37%) hydrochloric acid solution for one hour. Acid addition evolves some sulfur dioxide. After cooling, the pH was adjusted to 6 with 10 N sodium hydroxide and filtered to give a residue of ~25% of the original weight (mostly barium sulfate). The recovered barium (as barium chloride) represented 60% of the total barium carbonate sulfate residue reacted. That represented a barium recovery of 90-97%. This solution can be recycled with any necessary pH adjustments or evaporated to crystallize out barium chloride for reuse.

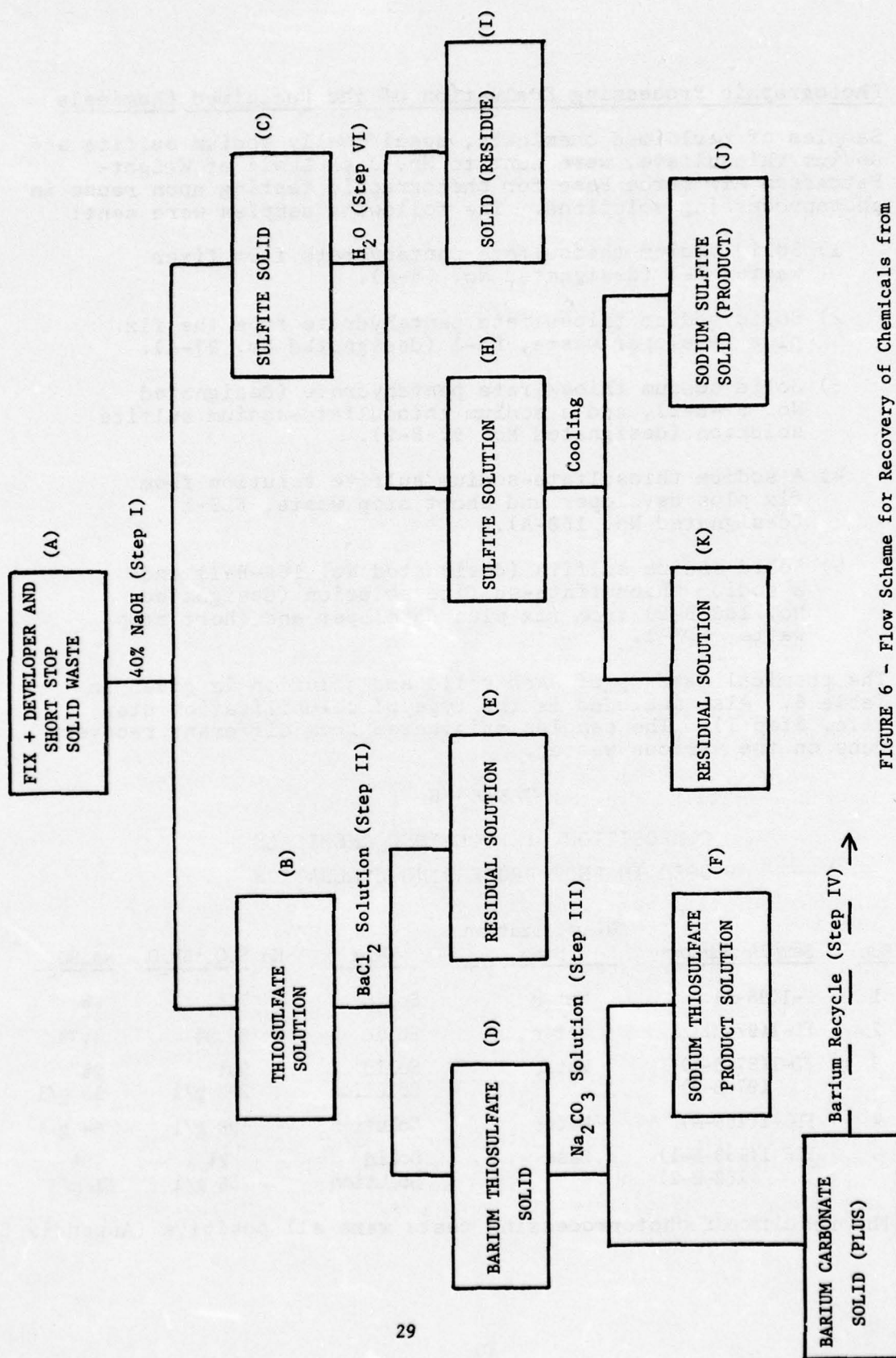


FIGURE 6 - Flow Scheme for Recovery of Chemicals from
Fix plus Developer and Short Stop

5. Photographic Processing Evaluation of the Reclaimed Chemicals

Samples of reclaimed chemicals, specifically sodium sulfite and sodium thiosulfate, were sent to Mr. Jack Lewis of Wright-Patterson Air Force Base for photographic testing upon reuse in photoprocessing solutions. The following samples were sent:

- 1) Solid sodium thiosulfate pentahydrate from fixer waste, F-1 (designated No. 96-A).
- 2) Solid sodium thiosulfate pentahydrate from the fix plus developer waste, FD-1 (designated No. 97-A).
- 3) Solid sodium thiosulfate pentahydrate (designated No. 97-B-1), and a sodium thiosulfate-sodium sulfite solution (designated No. 97-B-2).
- 4) A sodium thiosulfate-sodium sulfite solution from fix plus developer and short stop waste, FDS-1 (designated No. 168-A).
- 5) Solid sodium sulfite (designated No. 168-B-1) and a sodium thiosulfate-sulfite solution (designated No. 168-B-2) from fix plus developer and short stop waste, FDS-1.

The chemical make-up of each solid and solution is given in Table 6. Also included is the type of solubilization step (i.e. Step I). The samples originated from different recovery runs on the various wastes.

TABLE 6
COMPOSITION OF RECLAIMED CHEMICALS
USED IN PHOTOPROCESSING EVALUATION

Run	Sample Number	Solubilization Step	Type	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	Na_2SO_3
1	F-1(96-A)	Water	Solid	75%	6%
2	FD-1(97-A)	Water	Solid	86.9%	4.7%
3	FD-1(97-B-1) (97-B-2)	Water	Solid Solution	90% 280 g/l	2% 13 g/l
4	FDS-1(168-A)	Water	Solution	198 g/l	54 g/l
5	FDS-1(168-B-1) (168-B-2)	Base	Solid Solution	2% 158 g/l	78% 31 g/l

The results of photoprocessing tests were all positive (Appendix B).

6. Ozonation of Residual Solutions

A four liter sample of residual solution from fix plus developer (FD-1 plus FDS-1) test runs was placed in a contact column (4 ft. x 3 in. diameter). An air stream of 0.4% ozone was bubbled through the solution. Ozone production was 3 grams/hour. The pH was maintained between pH 8 and 13. The average air flow was 25 scfh. The COD was reduced from 64,000 mg/l to 30,000 mg/l in 60 hours. The solution went from dark brown to light yellow. At that point, the solution was evaporated to half its original volume and white crystals of sodium sulfate precipitated (120 grams).

7. Cost Analysis

The economics of the proposed method of reclamation of sodium thiosulfate and sodium sulfite is an important factor in the final recommendation. Chemical costs (shown in Appendix C) were used to determine cost benefits of the recovery. Table 7 shows the individual chemical costs and the total cost savings (based on a 1.135 kilogram sample) for recovery from fix plus developer waste (FD-1). The latter was used because it is one of the favored materials and the recommended process.

The reactions involved in this analysis are as follows:

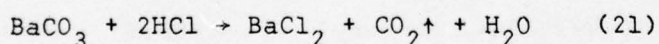
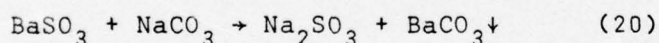
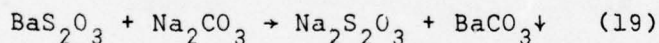
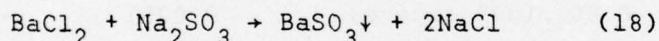
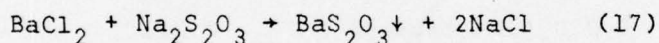


TABLE 7

CHEMICAL COSTS FOR RECLAMATION OF THIOSULFATE AND SULFITE
FROM A 1135 GRAM (2.5 LB.) SAMPLE OF FIX PLUS DEVELOPER WASTE (FD-1)

		- D O L L A R S -	
<u>Chemical</u>	<u>Amount (kg)</u>	<u>Cost/Kg</u>	<u>Savings (+) or Cost (-)</u>
<u>Recovered:</u>			
Na ₂ SO ₃	0.024	0.0454	+ 0.0011
Na ₂ S ₂ O ₃ ·5H ₂ O	0.724	0.0376	+ 0.0272
BaSO ₄	~0.115	0.1088	+ <u>0.0125</u>
Sub-Total			+ 0.0408
<u>Used:</u>			
BaCl ₂ ·2H ₂ O	0.490 (20% excess)	0.0639	- 0.0313
Na ₂ CO ₃ ·H ₂ O	0.220 (10% excess)	0.0118	- 0.0026
HCl (37%)	0.60 (50% excess)	0.0051	- 0.0031
H ₂ O	2.5	0.0002	- <u>0.0005</u>
Sub-Total			- 0.0375
<u>Recycled:</u>			
BaCl ₂ ·2H ₂ O	0.441 (90% recovery)	0.0639	+ 0.0282
H ₂ O	1.25 (50% recovery)	0.0002	+ <u>0.0002</u>
Sub-Total			+ 0.0284
Grand Total			+ 0.0317

The resultant cost total indicates that the process can at least pay for itself with the potential of a marginal profit.

SECTION VI

DISCUSSION OF RESULTS

The recovery of sodium thiosulfate and sodium sulfite from evaporated photographic wastes is possible. Other chemicals might be recoverable but were present in such low quantities in the samples received that recovery was not justified. The lower the concentration, the less economically justified is the recovery.

The combination of either water or basic solubilization followed by barium precipitation would allow for recovery of as high as 90% of the available sodium thiosulfate and as high as 60% of the available sodium sulfite (see Table 8).

TABLE 8
RECOVERY EFFICIENCY OF SODIUM THIOSULFATE AND
SODIUM SULFITE FROM PHOTOGRAPHIC WASTES

Waste	Solvent Type For Initial Solubilization	% Recovery	
		$\text{Na}_2\text{S}_2\text{O}_3$	Na_2SO_3
Combined (C-1)	Base	50-60	50-60
Fix Only (F-1)	Water	60-80	10-50
Developer Only (D-1)	Water	---	35-55
Fix + Developer (FD-1)	Water	80-90	10-50
Fix + Developer + Short Stop (FDS-1)	Base	35-50	45-55
Fix + Developer + Short Stop (FDS-1)	Water	50-60	10-20

The choice of water or basic solution solubilization is dependent on two factors:

- 1) The sodium thiosulfate content of the solid waste, and
- 2) the ratio of sodium thiosulfate to sodium sulfite.

Specifically, if the amount of sodium thiosulfate (as $\text{Na}_2\text{S}_2\text{O}_3$) is greater than or equal to approximately 50% of the total dry weight, water solubilization should be used. This allows direct isolation of a portion of the sodium thiosulfate as crystals by cooling. A caustic solution should be used in the initial solubilization step for sodium thiosulfate concentrations lower than 50%. The sodium sulfite present in the waste should be sufficiently low such that the ratio of sodium thiosulfate to sodium sulfite is not less than 3:1 for water solubilization. If this ratio is lower than 3:1, the choice should be caustic for sample solubilization.

From Table 9, it can be seen that the best mode of recovery is with fix alone or fix plus developer (and short stop) alone using water solubilization. That requires that the sodium thiosulfate concentration be greater than 50% of the waste. If this latter condition is not met, then operation on fix plus developer alone offers no advantage over using the combined waste. In all likelihood, if a combined waste containing greater than 50% sodium thiosulfate could be obtained, this might be the best approach (using water solubilization). This conceivably could give results comparable to the fix plus developer waste.

TABLE 9

PHYSICAL STATE OF CHEMICALS RECOVERED FROM PHOTOGRAPHIC WASTES

Waste	Type of Solubilization	Solid ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) Except Where Noted	Solution (Sodium Thiosulfate- Sodium Sulfite)
Combined (C-1)	Base	No	Yes
Fix Only (F-1)	Water	Yes	Yes
Dev. Only (D-1)	Water	Yes (Na_2SO_3)	No
Fix + Dev. (FD-1)	Water	Yes	Yes
Fix + Dev. + S.S. (FDS-1)	Base	Yes (Na_2SO_3)	Yes
Fix + Dev. + S.S. (FDS-1)	Water	No	Yes

It is apparent that in general the higher the concentration of sodium thiosulfate, the greater the recovery efficiency (see Table 10). This suggests that the recovery yields are essentially dependent only upon the mechanics of the recovery system, such as mixing efficiency, mixing time, reaction temperature, and separation techniques.

TABLE 10

RECOVERY EFFICIENCY AS RELATED TO
PERCENTAGE OF CHEMICAL PRESENT IN THE WASTES

Waste	- $\text{Na}_2\text{S}_2\text{O}_3$ -		- Na_2SO_3 -	
	% Present	% Recovered	% Present	% Recovered
Combined (C-1)	40	50-60	14	50-60
Fix Only (F-1)	57	60-80	7	10-50
Dev. Only (D-1)	--	--	17	35-55
Fix + Dev. (FD-1)	59	80-90	10	10-50
Fix + Dev. + Short Stop (FDS-1)	29-50	35-65	22-28	10-20

The same does not seem to be necessarily true for sodium sulfite which is present in much lower concentrations. Choice of water or caustic for the solubilizing solution makes a large difference as to the recovery efficiency of sodium sulfite.

The procedure that allows direct precipitation of crystalline chemicals (without chemical addition), namely sodium thiosulfate (as the pentahydrate) and/or sodium sulfite (as the heptahydrate) is the most desirable. This is true because the subsequent chemical treatment of the mother liquor (after crystallization) requires less chemicals and smaller volumes of solutions. In addition, the advantage of obtaining a crystalline solid that requires minimal purification is an obvious one for any end-user.

In a general scheme, both the barium and the water is recycled (see the flow scheme, Figure 7). The resultant products are sodium thiosulfate pentahydrate (solid and solution), sodium sulfite (solution) and barium sulfate. Recycling the water may cause build-up of organics and undesirable inorganics after a number of cycles and these would have to be discharged from the system. Possibly, only a percentage of the water could be reused to minimize this problem or the solution ozonated to decompose the organics and also precipitate sodium sulfate before recycling.

Sodium thiosulfate pentahydrate, sodium sulfite and barium sulfate are the main products as stated above. However, by varying the flow scheme, one can obtain also sodium sulfate (from ozonation of residual solutions), barium carbonate (if barium is not recycled), butyl acetate and quinone. A list of manufacturers of these chemicals is given in Appendix D. A list of users of these materials in industry is given in Appendix E.

SECTION VII

CONCLUSIONS

Sodium thiosulfate and sodium sulfite can be reclaimed from evaporated photographic wastes. Recovery efficiencies range from 35% to 90% for sodium thiosulfate and from 10% to 60% for sodium sulfite.

Developers, such as hydroquinone and elon, are present in such low concentrations that recovery is economically impractical. Sulfonated developers and their polymeric derivatives are present, and interfere with the isolation of recyclable chemicals. Conversion of those organics to recyclable quinone can be accomplished in low yields.

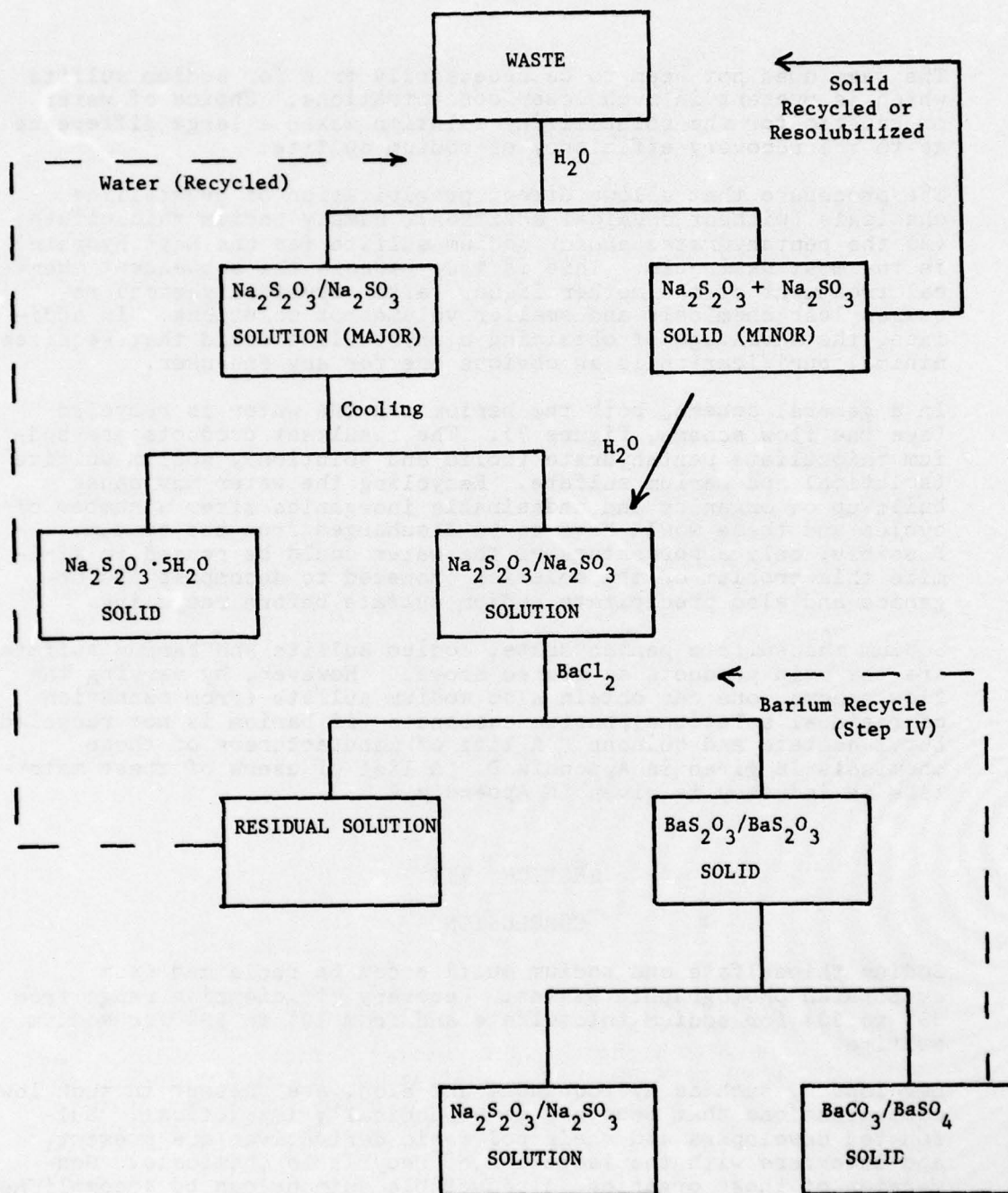


FIGURE 7 - General Flow Scheme for Recovery of Chemicals and Reuse of Chemical Agents

Acetic acid or sodium acetate can be reclaimed by conversion to butyl acetate followed by distillation.

Boron, phosphorous and metals such as silver, iron and cadmium are present in such small amounts that recovery is not practical.

Barium sulfate and sodium sulfate can be obtained as by-products of the recovery scheme.

A cost analysis indicates that the reclamation procedure for thio-sulfate and sulfite is cost effective. The recovery of barium ranges from 80-97% for the wastes examined.

It was found that if the concentration of sodium thiosulfate in any waste is greater than about 50% of the total and the amount of sodium sulfite is such that the ratio of sodium thiosulfate to sodium sulfite is greater than 3 to 1, then the recovery efficiency is enhanced. This is true because sodium thiosulfate can be precipitated as the pentahydrate directly from the solution resulting from solubilization of the waste.

For wastes containing less than 50% sodium thiosulfate and a ratio of sodium thiosulfate to sodium sulfite less than 3 to 1, water solubilization gives low recovery rates for both chemicals. It is, therefore, necessary to use concentrated sodium hydroxide solution solubilization of the waste. This affords separation of sulfite and thiosulfate and improved recovery of both over water solubilization.

Best recovery efficiencies are realized when the sodium thiosulfate concentration is above 50% of the total waste.

SECTION VIII

RECOMMENDATIONS FOR FURTHER WORK

1. General

In order to realize a substantial recovery efficiency of the predominant chemicals (sodium thiosulfate and sodium sulfite) found in evaporated photographic wastes, efforts should be made to maintain evaporated wastes that are at least 50% sodium thiosulfate (as $\text{Na}_2\text{S}_2\text{O}_3$). In the present study, this was only found to be true for sample F-1 and for one of the fix plus developer samples. If this condition (i.e. sodium thiosulfate >50%) can be met only by keeping the solutions separate prior to evaporation, that should become part of the standard handling procedure. If the combined waste provides concentrations of sodium thiosulfate greater than 50%, that is the preferred method of handling.

The desired reclamation procedure is then, that outlined previously in Figure 7. Of importance is the fact that this procedure calls for water solubilization, a process which is the reverse of the evaporation step. It might be advantageous to evaporate the waste down to a concentrated solution or slurry. This would require the use of less water in the recovery scheme, less energy in the evaporation state, and easier materials handling if the evaporation unit is in close proximity to the recovery equipment. In addition, less decomposition of the valuable chemicals might be realized.

2. Design of the Recovery Apparatus

The equipment and techniques required for recovery are standard in the chemical process industry. The basic steps are:

- 1) heating and mixing in a reaction vessel,
- 2) filtration,
- 3) cooling the mother liquor allowing crystallization,
- 4) filtration,
- 5) heating and mixing again in a reaction vessel and chemical addition with heating and mixing,
- 6) filtration,
- 7) heating and mixing of a solid and solution,
- 8) filtration, and
- 9) recycling of the barium.

This is shown in Figure 8.

Depending on the nature of the waste, grinding may have to precede the solubilization stage.

Manufacturers of the processing equipment needed are given in Appendix F.



FIGURE 8 - Recovery Process for Photographic Wastes

3. Developmental Work Required

The construction of a pilot plant system as described above is needed to develop a working system. This would give a much better picture of the recovery economics. Fabrication of a pilot plant requires investigation of proper large scale filtration systems, since each filtration technique has different chemical and physical requirements. The practical significant of recycling barium and water can only be determined in a pilot scale. Finally, scale-up recovery efficiencies must be determined.

The recovery of organics should be explored to determine methods of preserving these compounds such that larger quantities can be recovered.

It is, therefore, recommended that a follow-on study be conducted to determine these factors now that the general scheme has been determined.

APPENDIX A

ANALYTICAL PROCEDURES FOR EVAPORATED PHOTOGRAPHIC WASTES

Constituent	Analytical Method	
	Reference	Method
Sodium Sulfite (as Na_2SO_3)	Kodak B/W	BW-1308C
Sodium Thiosulfate (as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	Kodak B/W	BW-1308C
Boron (as B)	ANSI	Appendix A
Phosphorous (as $\text{PO}_4^{=}$)	Kodak	SLM-1152
Sulfate (as $\text{SO}_4^{=}$)	S.M.	156
<u>para</u> -Aminophenol (as Elon)	Kodak B/W	BW-407B
Hydroquinone (HQ)	Kodak B/W	BW-407B
Hydroquinone Monosulfonate (HQS)	Kodak B/W	BW-410F
Water (H_2O)	S.M.	148
Silver (Ag)	S.M.	129A
Iron (Fe)	S.M.	129A
Cadmium (Cd)	S.M.	129A

S.M. - "Standard Methods for the Examination of Water and Wastewater" (see Reference 1).

ANSI - "American National Standards Institute on Photographic Processing Effluents (see Reference 2).

Kodak B/W - "Chemical Control Procedures for Black-and-White Film Processing" (see Reference 3).

APPENDIX B

B-1 - TEST OF THE QUALITY OF RECLAIMED SODIUM THIOSULFATE FOR POSSIBLE REUSE IN PHOTOGRAPHIC FIXING FORMULA

1. Three one liter solutions of photographic fixer were mixed using Kodak Fixing Formula F-5.

Water at 120°F	800.0 cc
Sodium Thiosulfate (Allied Chemical Co.)	240.0 grams
Sodium Sulfite (Mallinckrodt)	15.0 grams
Acetic Acid 28% (Kodak)	48.0 cc
Boric Acid (Phillips & Jacobs)	7.5 grams
Potassium Alum (Fisher Scientific)	15.0 grams
Water to Make	1.0 liter

2. Solution #1 mixed from the above formula was used as the control throughout the series of tests.
3. Solution #2 mixed with reclaimed Sodium Thiosulfate Sample #96A.
4. Solution #3 mixed with reclaimed Sodium Thiosulfate Sample #97A.
5. The different Sodium Thiosulfates went into solution very rapidly, the only difference noted was the color of the solutions after mixing.

Solution #1 Control	-	Clear
Solution #2 Sample #96A	-	Light Tan
Solution #3 Sample #97A	-	Light Yellow

6. pH of the resultant formulas at room temperature (68°F).

Solution #1 Control	-	3.7
Solution #2 Sample #96A	-	3.6
Solution #3 Sample #97A	-	3.7

7. Samples of unexposed film (Kodak 3414 and Kodak SO-192) cleared within 10 seconds in each of the three Fixing Solutions.
8. Sensitometric and Resolution Target Exposures were made from samples of Kodak 3414 and Kodak SO-192 films. Processing was in D-19 for 8 and 5 minutes. Acetic Acid short stop for 30 seconds. Two samples of each film were fixed for 5 minutes in each of the test solutions.
9. Using the Taber Shear-Scratch Tester Model 203 the emulsion hardness of processed samples of Kodak 3414 and Kodak SO-192 were checked after fixing in each of the three test Fixing Solutions, NO NOTICEABLE EFFECT WAS NOTED.

A.C. Zonars
AFAL/RWF/7 Oct. 75

TEST NO. _____ QUANTASCAN C - AUTOMATIC RECORDING DENSITOMETER
 DATE 10/10/75 MATERIAL 3114 EMULSION NO. 2414-17-3 EXP. EQUIP. 1 B. 8. 1. EXP. TIME 1/5 Sec. FILTER 61000K
 DEV. EQUIP. HSB TYPE DEV. D-19 DEV. TIME 8 Min. DEV. TEMP. 68°F PREPARED BY A. G. GONOFF

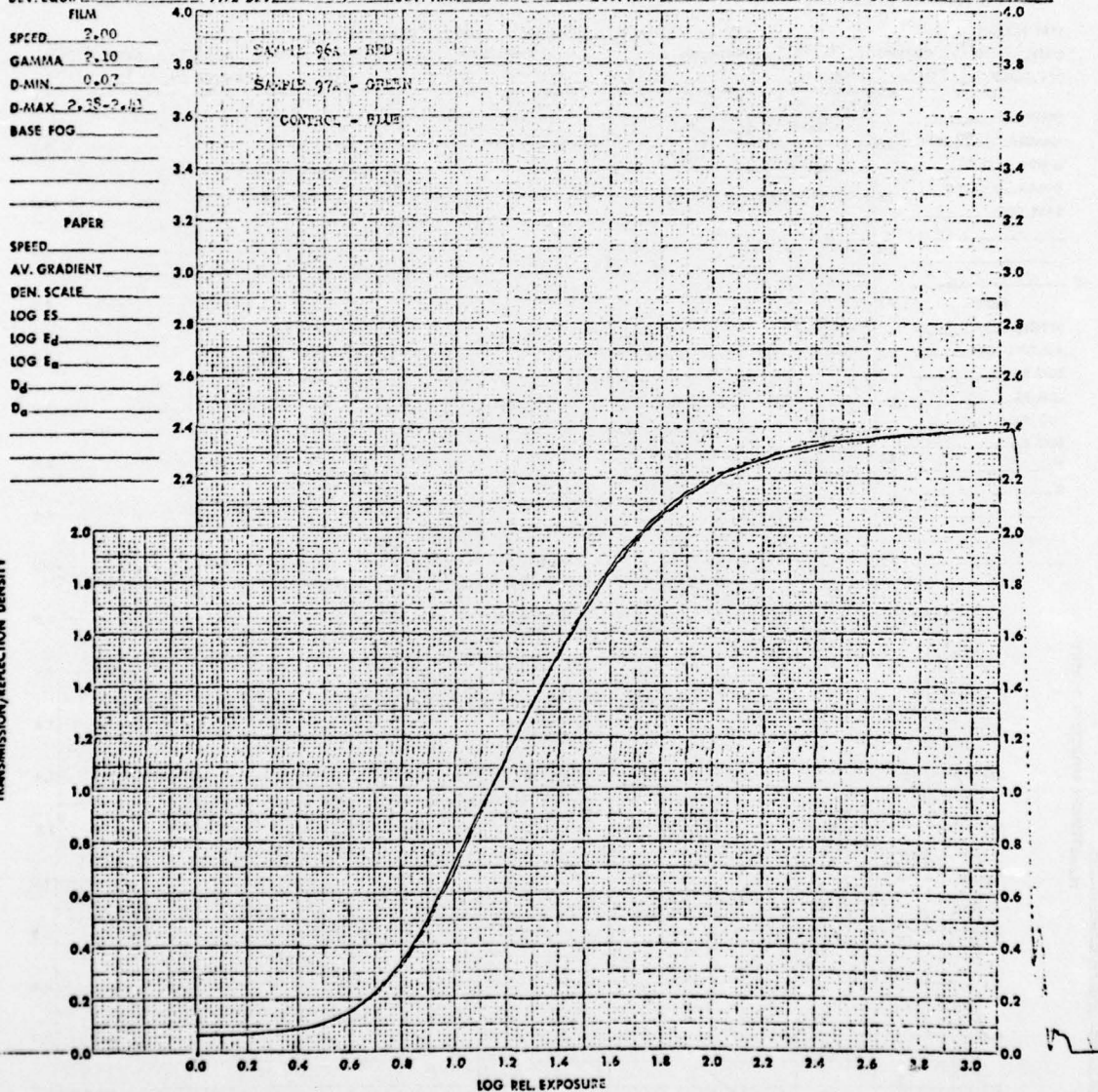


CHART NO. ODI-624-PP QUANTAMETRIC DEVICES, INC., JOHNSON CITY, N.Y.

DEV. EQUIP. High TYPE DEV. D-10 DEV. TIME 5 min. DEV. TEMP. 60° PREPARED BY A. C. Stevens

FILE# 4.0

GAMMA 1.20 3.8

D-MAX 2.15-2.20

[illegible]

SPEED

DEN. SCALE

LOG E₁ 2.8

2.6

24

[illegible]

Year	Percent
1950	7.0
1955	8.0
1960	9.0
1965	10.0
1970	11.0
1975	11.5
1980	12.0

[illegible][illegible]

1.4

[illegible]

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	5
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APPENDIX C
COST OF CHEMICALS

<u>Chemical</u>	<u>Cost (\$/lb)</u>	<u>Cost (\$/kg)</u>
Sodium Thiosulfate Pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	0.083	0.0376
Sodium Sulfite (Na_2SO_3)	0.010	0.0045
Hydrochloric Acid (HCl, 37%)	0.011	0.0050
Barium Chloride Dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$)	0.141	0.0639
Sodium Carbonate, Anhydrous (Na_2CO_3)	0.026	0.0118
Barium Sulfate (BaSO_4)	0.240	0.1088
Sodium Sulfate (Na_2SO_4)	0.041	0.0186
Water (H_2O)	---	0.0002

The prices listed are for car-lot amounts.

APPENDIX D
CHEMICAL MANUFACTURERS

Sodium Thiosulfate Pentahydrate

Allied Chemical, Ind. Chem. Div., Solvay, N.Y.; N. Claymont, Del.; Chicago, Ill.; El Segundo, California.

Ferro Corp., Baton Rouge, La.

Stauffer Chemical Co., South Gate, California.

Sodium Sulfite

Allied Chemical Corp., Ind. Chem. Div., Solvay, N.Y.

J.T. Baker Chemical Co., Phillipsburg, N.J.

Mallinchrodt Chemical Works, St. Louis, Mo.

Sodium Sulfate

Alazone, Inc., Enka, N.C.; Lowland, Texas.

Allied Chemical Corp., Baltimore, Md.

American Cyanamide Co., Fort Worth, Texas.

Beaunit Corp., Elizabethton, Tenn.

Climax Chemical Co., Monument, N.M.

Hercules, Inc., Glens Falls, N.Y.

FMC Corp., Nitro, West Virginia.

Mallinchrodt Chemical Works, St. Louis, Mo.

Barium Carbonate

Allied Chemical Co., Marcus Hook, Pa.

J.T. Baker Chemical Co., Phillipsburg, N.J.

Barium and Chemicals, Inc., Steubenville, Ohio.

Chemical Products Corp., Cartersville, Ga.

FMC Corp., Modesto, California

Sherwin-Williams Co., Coffeyville, Kansas.

Barium Sulfate

J.T. Baker Chemical Co., Phillipsburg, N.J.

Barium and Chemicals, Inc., Stuebenville, Ohio.

Mallinchrodt Chemical Works, St. Louis, Mo.

Butyl Acetate

Alanese Corp., Bishop, Texas.

Commercial Solvents Corp., Terre Haute, Indiana.

Tennessee Eastman, Kingsport, Tennessee.

Union Carbide Corporation, Institute, W. Va.;

S. Charleston, W. Va.; Texas City, Texas.

Quinone

Eastman Kodak Co., Chemical Products Div., Rochester, N.Y.

Mobay Chemical Co., Naftone Div., New York, N.Y.

APPENDIX E

USES OF RECOVERED CHEMICALS (SOURCE)

Sodium Thiosulfate Pentahydrate

Photography; chrome tanning; removing chlorine in bleaching and papermaking; extraction of silver from its ores; dechlorination of water; mordant in dyeing; reagent in analytical chemistry; medicine; bleaching bone, straw, ivory; reducing agent in chrome dyeing.

Photographic Industry	90%
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Others	10%
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Sodium Sulfite

Dyes; intermediates; organic chemicals; sodium thiosulfate; textiles (bleaching delicate fabrics, antichlor); chemical reducing agent; preservative; photography (developer); engraving and lithography; medicine; silvering mirrors; treating rubber latex; sterilizing beer kegs; permanent wave solutions.

Sodium Sulfate

Manufacturing of kraft paper; paperboard; glass; water glass; sodium salts; ceramics glazes; processing textile fibers, dyes and soaps; tanning stock; pharmaceuticals; freezing mixtures; detergent composition.

Kraft Paper Mfg.	70%
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Synthetic Detergents	20%
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Glass Mfg. and Miscellaneous	10%
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Barium Carbonate

Rat poison, optical glass, flat wall paint, foundry core cpd., water purification, ceramics, marble substitutes, dyes, enamels for ironware, rubber, beet sugar.

Other Barium Chemicals	33%
Glass	25%
Brick & Clay Products	25%
Barium Ferrites	4%
Miscellaneous	13%

Barium Sulfate

Reagent for paints; filter for textiles, rubber, linoleum, oil-cloth, plastics and lithograph inks; base for lake colors, indicator in X-Ray photography.

Butyl Acetate

Solvent for lacquers, lacquer enamels, pyroxylin solutions, leather dope, airplane dope, perfumes, flavouring extracts; solvent for natural gums and synthetic resins.

Protective Coatings	60%
Solvent Use & Export	40%

Quinone

Manufacturing of dyes and hydroquinone.

APPENDIX F
CHEMICAL PROCESS EQUIPMENT MANUFACTURERS

Stirrers

Bench Scale Equipment Co., Inc. Div. of Chemineer, Inc.,
1517 E. 4th Street, Dayton, Ohio 45401.

Mixing Equipment Co., 135 Mt. Read Blvd., Rochester, N.Y.

Reaction Vessels

Bench Scale Equipment Co., Inc. Div. of Chemineer, Inc.,
1516 E. 4th Street, Dayton, Ohio 45401.

Separation Equipment (Filter, Centrifuges)

Demso, Inc., 819-845 S.E. 29th St., Oklahoma City, Ok. 73109.

Filterite Corp., Timonium, Md. 21093.

Trumpler-Clancy, Inc. (Industrial Filtration Engineers),
Box 509, Hamburg, New York 14075.

Extraction and Solvent Recovery Equipment

Chem-Pro Equipment Corp., 27 Daniel Road, Fairfield, N.J. 07006.

Erie Universal Products Co., 311 State St., Erie, Pa. 16507.

Sulfur Dioxide Scrubbers

Koch Engineering Co., Inc., Static Mixing Div., 161 East 42nd
Street, New York, New York 10017.

Croll-Reynolds Co., Inc., 751 Central Ave., Westfield, N.J. 07091.

Grinding, Dry Chemical Feeders, Equipment

Alpine American Corp., 3 Michigan Drive, Natids, Ma. 01760.

Chem Grout, Inc., P.O. Box 1140, LaGrange Park. Il. 60525.

Mechanical Development Corp., Whitewater, Wis. 53190.

Evaporators (and Sludge Dehydration Equipment)

Koch Eng. Co., Inc., 161 E. 42nd St., New York, N.Y. 10017.

Ozark-Mahoning Co., 1870 S. Boulder, Tulsa, Ok. 74119.

Idrex, Inc., 127655 S. Western Ave., Blue Island, Il. 60406.